

AD-A196 998

(4)

PORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS DTIC FILE CODE	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Unclassified/Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report 20		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research, Resident Rep.	
6a. NAME OF PERFORMING ORGANIZATION Corrosion Research Center	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) Federal Building, Room 286 536 South Clark Street Chicago, IL 60605-1588	
5c. ADDRESS (City, State, and ZIP Code) University of Minnesota Minneapolis, MN 55455	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-85-1588		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable) Code 1113	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		11. TITLE (Include Security Classification) Lithium Secondary Batteries: Role of Polymer Cathode Morphology	
12. PERSONAL AUTHOR(S) Katsuhiko Naoi, Tetsuya Osaka and Boone B. Owens			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 7/15/85 TO 5/30/88	14. DATE OF REPORT (Year, Month, Day) June 1988	15. PAGE COUNT 2
16. SUPPLEMENTARY NOTATION Paper to be presented at the 174th National Meeting of the Electrochemical Society, Chicago October 1988			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) conducting polymers, polypyrrole, lithium cells. (main)	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Electrically conducting polymers have been utilized both as the cathode and as the electrolyte element of Li secondary cells. Polymer cathodes were limited in their suitability for batteries because of the low energy content associated with low levels of doping and the inclusion of complex ionic species in the cathode. Recent studies have indicated that doping levels up to 100 percent can be achieved in polyaniline. High doping levels in combination with controlled morphologies have been found to improve the energy and rate capabilities of polymer cathodes. A morphology-modifying technique was utilized to enhance the charge/discharge characteristics of Li/liquid electrolyte polypyrrole cells. The polymer is electropolymerized in a preferred orientation morphology when the substrate is first precoated with an insulating film of nitrile butadiene rubber (NBR). Modification of the kinetic behavior of the electrode results from variations in the chemical composition of the NBR. Further improvement in kinetic behavior of polymer cathodes should result from continuing investigations of these phenomena.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Boone B. Owens		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL (612) 625-1332	

Lithium Secondary Batteries: Role of Polymer Cathode Morphology

Katsuhiko Naoi^{*,**}, Tetsuya Osaka^{**} and Boone B Owens^{*}

^{*} Corrosion Research Center, Dept. of Chem. Eng.,
University of Minnesota, 112 Amundson Hall, 221 Church St SE,
Minneapolis, MN 55455

^{**} Dept. of Appl. Chem., Waseda Univ., 3 Okubo, Shinjuku, Tokyo
160, JAPAN

Promising cathode materials for rechargeable lithium electrochemical cells include solid intercalation compounds such as metal oxides or sulfides and electroactive, polymer cathode materials such as polyaniline or polypyrrole. The theoretical values for the specific energy of the electrode couples may be calculated for these two classes of cathodes; the solid oxide type cathodes exhibit theoretical specific energies in the range of 300-1000 Wh/kg, compared to values of about 200-400 Wh/kg for the polymeric cathode materials. Lithium/polymer cathode cells have intrinsically lower values for specific energy because of the low doping level of the polymer films and the requirement of ionic doping associated with the faradaic reaction. Further, slow ion diffusion within the bulk of the polymer films results in limitations on the rate behavior of such cell systems.

An electrochemically-formed conducting polymer film of polypyrrole (PPy) has been grown on an electrode substrate; when the substrate is precoated with a film of nitrile butadiene rubber (NBR), a highly enhanced anion doping-undoping process results because of the oriented-growth structure. This is illustrated in Figure 1 which shows that the polypyrrole cathode materials are grown as continuous fibers or dendrites normal to the plane of the electrode (Ref 1). In order to prepare this high surface area electrode structure, the NBR film is solvent cast onto the surface of the electrode. When this insulated electrode is inserted in the electrolyte solution (for example, LiClO₄ in acetonitrile) the NBR film is partially dissolved. As channels are opened up due to this dissolution, the electropolymerization of the pyrrole initiates at the electrode surface. The polypyrrole film then deposits in the direction perpendicular to the substrate, forming within the matrix of the NBR host-polymer. The guest PPy polymer grows through the fine channels etched by the penetration of the electrolyte into the NBR film during electropolymerization as shown in Figure 2. The host polymer of NBR film is subsequently removed in order to leave the backbone of the precipitated PPy film.

Potential step and AC impedance measurements for these electrodes demonstrate that the NBR/PPy electrode exhibits a faster anion doping process than an ordinary PPy electrode (Ref 1). Inspection of the surface of the film by Scanning Electron Microscopy revealed that the PPy film grown directly on platinum substrate exhibits a relatively compact structure of approximately 1 μ m thickness. In contrast the PPy film formed by the NBR process exhibited a porous open structure with a thickness of about 2-3 μ m when equivalent amounts of polymer were deposited (1 coulomb/cm²).

The polypyrrole exhibits a doping level of about 33 percent and this cathode has been developed into a commercial battery design (Ref 2). More recently polyaniline (PAN) was reported to exhibit a doping level in excess of 80 percent (Ref 3); this results in an increase in the theoretical specific energy for a cell system utilizing such a cathode. The Li/PAN system has also been recently reported in a commercial battery development (Ref 4). With advances in the doping levels and also the ability to control the morphology in a manner that enhances the rate capability,

there is renewed interest in lithium/polymer cathode cell systems. Although they do not appear to be capable of achieving the theoretical specific energies of the solid intercalation cathodes, under certain conditions they may exhibit superior values for the power density in energy storage devices.

References

1. Naoi, K. and Osaka, T., J. Electrochem. Soc., **134** 2479 (1987).
2. "Electrically Conductive Polymers As Rechargeable Battery Electrodes," D. Naegele and R. Bittu, Abstract No. A5-3, Extended Abstracts, p. 310, 6th International Conference on Solid State Ionics, Garmisch-Partenkirchen, September 6-11, 1987.
3. Ishihara et al., CRIEPI report T86055 (1987).
4. Ogawa et al., The 27th Battery Symposium Japan, p. 197 (1986).

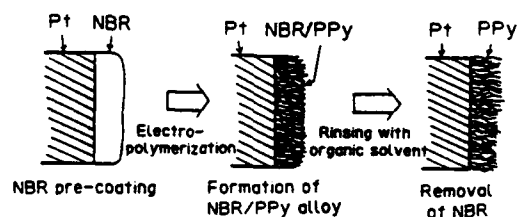


Fig.1 Preparation procedure of NBR/PPy film

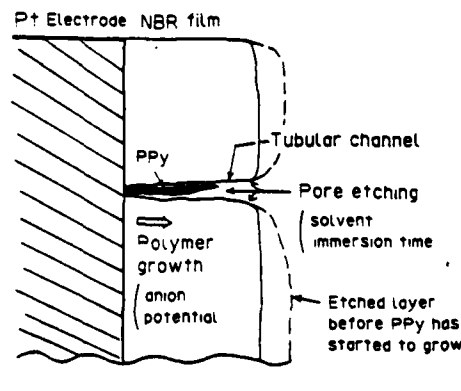


Fig.2 Schematic model for tubular channel formation into NBR film and polymer growth through it.



By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	